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## FATE AND EFFECT OF ARSENIC APPLIED AS A SPRAY FOR WEEDS

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### INTRODUCTION

In certain districts of Hawaii during the rainy season cultivation is impracticable, because of its bad effect upon the texture of the soil. Yet at times this season is abnormally long and especially favorable to the growth of weeds. Weed control is therefore a very important problem for Hawaiian planters. In experiments at the Hawaii Experiment Station<sup>1</sup> it was found that the most economical means of weed control under such conditions lay in the use of chemical sprays. Careful comparative tests were made of such chemicals as sodium arsenite, ferrous sulphate, carbon bisulphid, etc. Of these, sodium arsenite proved by far the most effective and was recommended for use. Sodium arsenite sprays have now been used in Hawaii for weed eradication for about five years and have proved to be efficient and economical. Such sprays have not only been used to replace hand labor in the fields, but also as a means of ridding grass lands of undesirable plants.

In view of the possible injury to soils and crops as a result of the continued use of such sprays, the Hawaii Experiment Station undertook a study of the fate in the soil of the arsenic so applied and its influence upon plant growth and upon ammonification and nitrification.

### EFFECT OF SODIUM ARSENITE ON PLANT GROWTH

Apparently there is little or no immediate danger to crops from the use of sodium arsenite as a spray. In fact, in experiments with millet, buckwheat, and cowpeas grown on three different types of Hawaiian soils it was found that small quantities of arsenic stimulate plant growth. However, analyses of the plants did show that the arsenic is assimilated and that when it is present in the tissues in sufficient concentration death of the plant results.

The most surprising feature of the investigation was the influence on the ammonifying and nitrifying bacteria. In one type of soil ammonification was stimulated even by such excessive amounts as 1 per cent of arsenic ( $As_2O_3$ ) in the soil. The results as a whole indicate that no fear need be entertained regarding any detrimental influences toward the

<sup>1</sup> Wilcox, E. V. Killing weeds with arsenite of soda. Hawaii Agr. Exp. Sta. Press Bul. 30, 15 p. [1911.]

Krauss, F. G. Suppression of weeds among pineapples by arsenite of soda spray. Hawaii Agr. Exp. Sta. Press Bul. 48, 8 p., 3 fig. 1915.

McGeorge, W. T. The effect of arsenite of soda on the soil. Hawaii Agr. Exp. Sta. Press Bul. 30, 16 p., 3 fig. 1915.

organisms upon which the plants rely for their available nitrogen, provided proper soil texture is maintained.

Furthermore, it was found that in time the arsenic practically loses its toxic influence toward plants. This was shown by the comparative growth of plants on soils treated at time of seeding and those seeded several months following the application of the arsenic to the soil. There are only two possible explanations of this condition: Either the arsenic reacts with certain of the soil constituents, resulting in a less toxic combination, or it is rapidly leached from the soil.

#### ABSORPTION OF ARSENIC BY THE SOIL

When a soluble salt is added to a soil, its ultimate disposition must depend upon certain chemical reactions and physical phenomena. In this case the possibilities involve (1) a combination with or replacement of salts already present, resulting in its absorption as a whole; or (2) a selective absorption involving the fixation of only one ion of the salt.

In order to determine the fate of arsenic and the effect of irrigation, a set of lysimeter experiments was inaugurated.

#### LYSIMETER EXPERIMENTS

Three types of soil were selected: (1) A ferruginous red clay, (2) a ferruginous brown clay, and (3) a highly organic silt. Twenty-five pounds of soil were placed in each of six lysimeters, two being filled with each type. To each soil were added 3 liters of a solution of sodium arsenite of the same strength as that used for spraying weeds. One series of three was allowed to stand for two months protected from rain. To the other three 1 liter of water was added every other day for several weeks, after which the soil was allowed to stand in the lysimeter until dry enough to sample.

The object of these experiments was to determine the rate of fixation, the depth to which the arsenic can penetrate, and the leaching effect of irrigation. At the expiration of the above time samples were taken at various depths in the lysimeters and the percentage of arsenic ( $As_2O_3$ ) in the soil at each depth was determined. The results are given in Table I.

TABLE I.—Effect of irrigation on arsenic in the soil, giving the percentage of arsenic at various depths

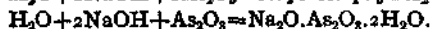
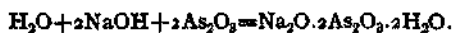
Soil No. 1.			Soil No. 2.			Soil No. 3.		
Depth.	Not irrigated.	Irrigated.	Depth.	Not irrigated.	Irrigated.	Depth.	Not irrigated.	Irrigated.
Inches.	Per cent.	Per cent.	Inches.	Per cent.	Per cent.	Inches.	Per cent.	Per cent.
1 to 3	0.280	0.224	1 to 3	0.450	0.237	1 to 2	0.97	0.95
3 to 5	.198	.211	3 to 5	.170	.092	2 to 4	.50	.47
5 to 7	.171	.145	5 to 7	.118	.092	4 to 6	0	0
7 to 9	.184	.170	7 to 9	.013	.....	.....	.....	.....

The columns headed "Not irrigated" show the percentage of arsenic in the soil at the given depth in the lysimeters which were protected from rain and which received no irrigation. The columns headed "Irrigated" show the percentage of arsenic in the soil at the given depth in the lysimeters which were subjected to irrigation. A comparison of the two columns for each soil will show the strong fixing power of these soils for arsenic, the influence of different soil types upon the fixation, and the danger of its accumulation. Samples of soil No. 3 were taken at depths different from those of soils Nos. 1 and 2, as shown in Table I, because of the concentration of arsenic at the surface in the former.

In order to determine how nearly these results represent actual field conditions, samples of soil were obtained from a plantation at Nahiku, Maui, which was the first to adopt the use of sodium arsenite as a means of weed control. Weeds on this land have been sprayed for five years, at the rate of three applications per year, using 5 pounds of arsenic ( $As_2O_3$ ) per acre for one application. During this time the soil has received no cultivation whatever and the rainfall averages about 200 inches per year. The soil is very porous and there is very little run-off water. Samples were taken at three depths: Every 4 inches of the first foot. The surface 4 inches contained 0.00924 per cent of arsenic ( $As_2O_3$ ), and none was present below this depth. A determination made by boiling the soil with water showed an arsenic content of 0.00006 per cent, or 0.6 p. p. m., soluble in water. That the arsenic fixed by soils in the lysimeters was partly soluble in water indicates that the fixation is due in part to physical influences.

#### CHEMICAL REACTIONS INVOLVED IN THE FIXATION

The composition of the spray as prepared by recommended methods may be either a solution of the acid salt ( $Na_2O \cdot 2As_2O_3 \cdot 2H_2O$ ) or the neutral salt ( $Na_2O \cdot As_2O_3$ ), depending on the proportions of soda (either hydrate or bicarbonate) and arsenious acid used.



For the following experiments in studying the replacement phenomena, a solution of the neutral salt was used.

One liter of a 1 per cent solution of sodium arsenite was allowed to act upon 200 gm. of soil, with occasional shaking, for two weeks. Checks were also maintained with 200 gm. of soil and 1 liter of water. The arsenic extract was then separated from the soil and a partial analysis made to determine the elements with which the sodium arsenite is most active. The results are given in Table II, which shows the composition of a 1 per cent sodium-arsenite solution after contact with the soil, as compared with the solvent action of water. The percentage of humus

in the soil before and after treating with 1 per cent of sodium arsenite is also given.

TABLE II.—Composition of the extracts (mgm. per liter)

Constituent.	Soil No. 1.		Soil No. 2.		Soil No. 3.	
	Water extract.	Arsenic extract.	Water extract.	Arsenic extract.	Water extract.	Arsenic extract.
Fe <sub>2</sub> O <sub>3</sub> .....	Trace.	716	Trace.	121	Trace.	90
CaO.....	11.2	84	13.6	124	74.6	126
MgO.....	3.6	20	10.8	44	7.4	36
As <sub>2</sub> O <sub>3</sub> .....		3,960		6,000		4,480
Mg.As <sub>2</sub> O <sub>3</sub> fixed by 100 gm. soil.....		2,640		600		2,120
Humus I <sup>a</sup> , per cent.....	2.77		1.68		8.75	
Humus II <sup>a</sup> , per cent.....	1.56		1.80		8.40	

<sup>a</sup> Humus I shows the percentage of the humus content of original soil; humus II, that of soil after treatment with the 1 per cent sodium-arsenite solution.

Table II shows a replacement of and a solvent action toward iron, calcium, magnesium, and humus, and suggests several theories as to the nature of the reaction. The soil absorbing the largest amount of arsenic lost through solution or replacement the most iron and humus. The soil absorbing the least arsenic lost the least iron and no humus. Apparently the absorption of arsenic by soil No. 3 is largely a mechanical fixation, as the data show a high absorption, but a low replacement.

In sodium arsenite we have the combination of a strong base with a weak acid. A well-known property of such salts is to react alkaline when dissolved in water. This is due to the faint dissociation of H<sub>2</sub>O into H<sup>+</sup> and OH<sup>-</sup> ions. Here the chemical and physical phenomena involved in the fixation of sodium arsenite are directly or indirectly a result of hydrolysis. The latter term as used herewith is intended to convey the increased dissociation in a solution of sodium arsenite, which itself is only faintly dissociated. This results in an increase in the concentration of the hydroxyl ion and the formation of the highly dissociated electrolyte sodium hydrate, which in the soil would probably be rapidly converted to bicarbonate. In this form it would have a solvent action toward the iron and humus and more or less toward the magnesium and calcium through the formation of slightly soluble bicarbonates. Magnesium bicarbonate is very unstable as compared to calcium bicarbonate and, hence, is precipitated following the solvent action of the sodium bicarbonate. The calcium is more soluble even in the soils containing much higher amounts of magnesium. These reactions leave the arsenic free as the negative ion to combine with the dibasic and tribasic metals to form slightly soluble arsenites or arsenates, thereby fixing the arsenic in the soil.

The rate and extent of fixation of arsenic vary in different soil types, owing to the concentration and solubility of the basic constituents—i. e., dissociation was found to be more rapid in some soils than others. To illustrate, the soil absorbing the greatest amount of arsenic exhibited the strongest alkalinity and showed the greatest chemical activity. Furthermore, this same soil contained the least amount of the soluble bases, calcium, magnesium, and potassium, indicating that the chemical fixation is influenced by the pressure of soluble bases.

#### SUMMARY

It has been shown herein that soils possess strong fixing power for arsenic and that when a sodium-arsenite spray is used for destroying weeds the arsenic will ultimately be deposited in the surface soil, there to remain in spite of the leaching effect of rains or irrigation.

The chemical reactions involved in the fixation are a replacement or solution of iron, calcium, magnesium, and humus, owing in part to a hydrolysis of the sodium arsenite in solution, also a combination with the dibasic and tribasic elements to form the difficultly soluble arsenites or arsenates.